— 2003 IMF Review

Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations

Jeff Goodwin, Gary Gray

Tina M. Nenoff, Mutlu Ulutagay-Kartin, Chris Cornelius,

Thomas M. Anderson

June 25, 2003

Sandia National Laboratories

GOODYEAR CHEMICAL

Nofsinger

— Agenda

- Team Members
- Background
- Project
  - Description and Goals
  - Milestones
  - Funding
  - Benefits
- Technical
- Summary

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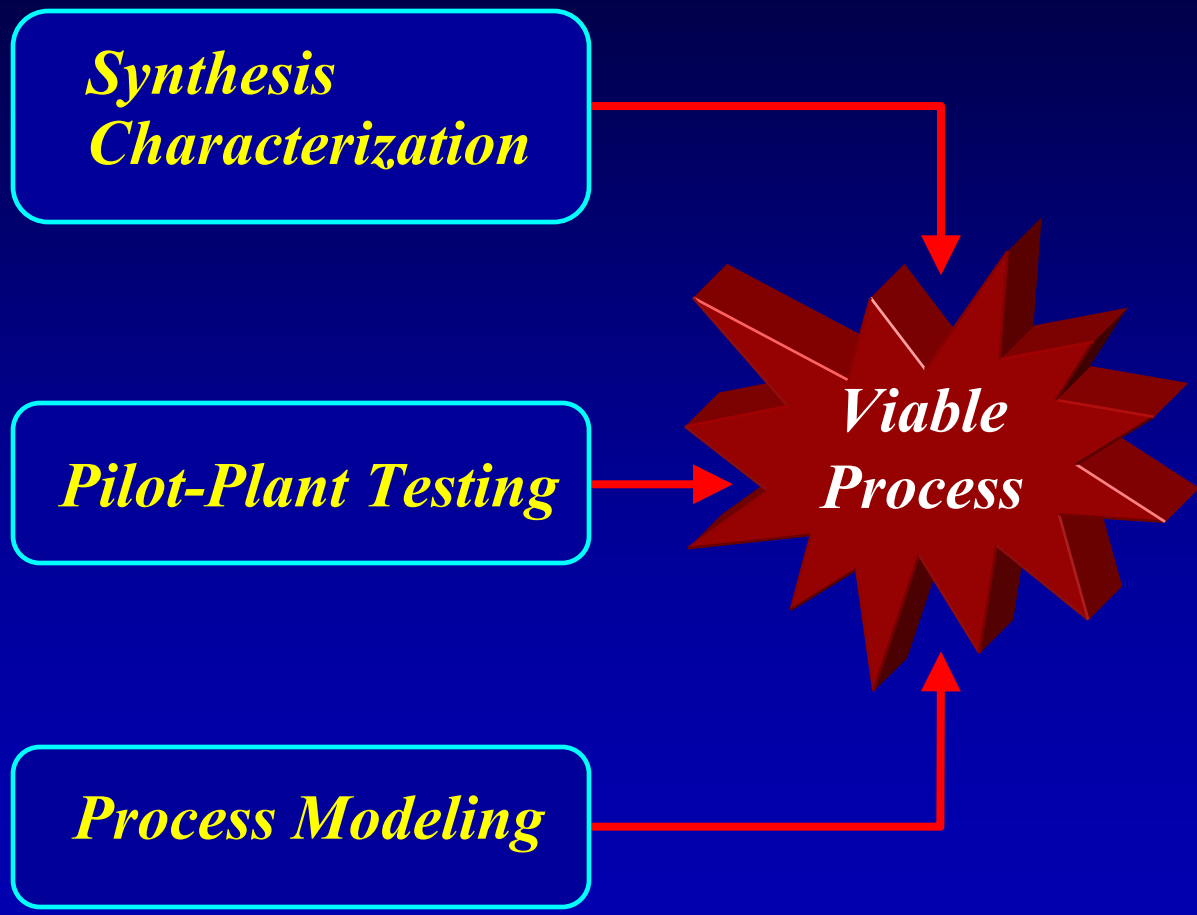
— Research Team

Sandia National Laboratories
Tina M. Nenoff
Mutlu Ulutagay-Kartin
Chris Cornelius

Goodyear Chemical
Jeff Goodwin
Gary Gray

Nofsinger
Tom Anderson
Geoff Stephenson



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— Background/Business Case

Objective: Reduced Energy Consumption Using Membranes

Current Isoprene Monomer Technology

Feedstock

15-60% Isoprene
6-19% Isopentane
7-20 % n-Pentane
10-20% 1-Pentene, etc.

Isoprene Unit

Isoprene (99+%)

- PI
- Specialty Polymers
- External Sales

Feed for Hydrocarbon Resins:
Pentadiene (55%)
2-MB-2 (15%)

→ Wingtack Product

Raffinate

→ External sales to "gas pools"

★ Potential Separation Location

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— DOE/IMF Project Description & Goals

Description

Create materials for Energy Efficient HC separations

- Scientific focus on surface modified zeolites
- Enrichment / separation of isoprene from C5 stream
- Separations to provide basis of application toward other energy-intensive C2-C5 separation processes

Goals

- Develop new membrane materials or separation-based adsorbents via modification of commercially-available zeolites
- Establish zeolite structure-property models for this technology & others
- Decrease energy consumption in the chemical & petroleum industries by employing these new & improved materials

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—Goodyear and Sandia Project Milestones

Milestones

Yr1: Zeolite Modification and testing; Go/No Go
Initial Economic Analysis

Yr2: Selection of "best" modified zeolite through characterization and testing; large scale synthesis

Yr3: Pilot Plant testing, material modification;
In-depth economic calculations;
Engineering Analysis

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— DOE/OIT/IMF Project Funding

"Novel Modified Zeolites for Energy-Efficient Hydrocarbon Separations"

Collaborative Research

198K/yr OIT/IMF "Direct to SNL"
188K/yr **Goodyear** "In-Kind"
10K/yr **Nofsinger** "In-Kind"

$1.2M / 3yr program (FY02-04)
50% "in-kind" industry funding,
commenced 4/23/2002.

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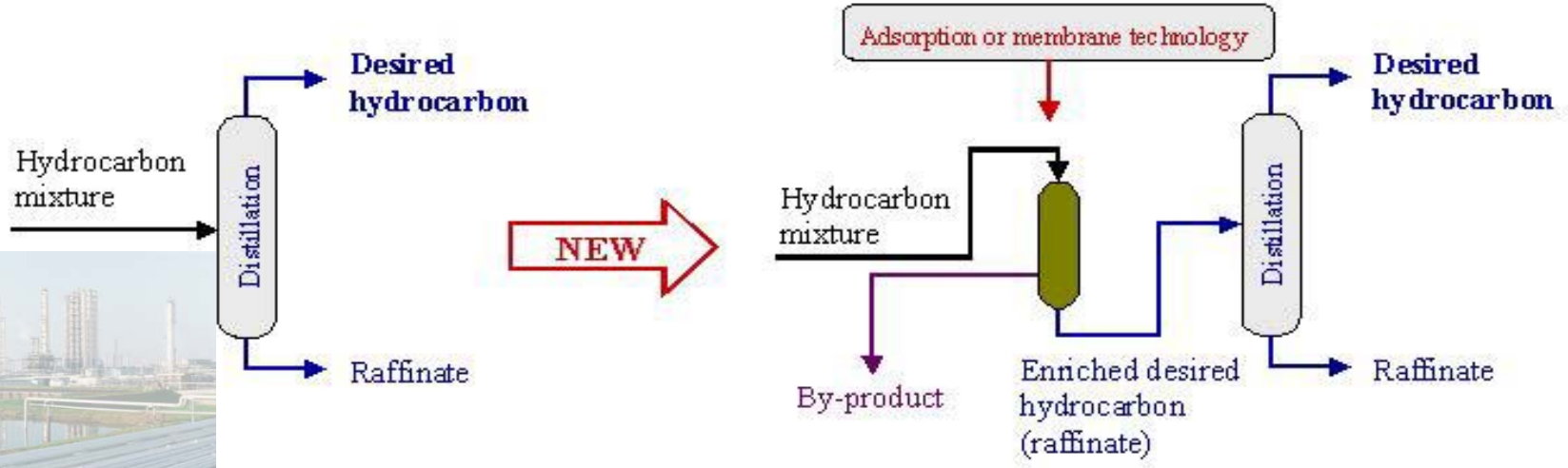
Potential Benefits to Goodyear: Energy Savings

***Need:** Process Improvement for Isoprene Separation*

Current Technology	**Proposed Technology** Adsorption or Membrane Separation
	22% Reduction in Energy



Energy Intensive	**Less Energy Intensive**

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— Potential Energy Benefits to U.S. Chemical Industry

- Goodyear is domestic leader in isoprene production (60%).
- Economic Modeling from Nofsinger shows 22% reduction in Energy of Isoprene Process Using modified Zeolites (membranes). Goodyear saves 1 trillion Btu/yr.
- Extrapolation to C_2-C_5 industries predicts 64 Trillion BTU's savings

	Btu/yr Trillion	2002 Billion lbs	Btu/lb
Ethylene- C2	214	53	4,058
Propylene- C3	53	39	1,359
Butadiene- C4	21	4	5,366
Isoprene- C5	5	0.4	8,000+
Total	293		

22 % Reduction

64 Trillion Btu's

Source: CMAI - 2003

DOE/OIT Energy & Environ. Profile 2002

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— Technical Section: Previous Technology Review

- Current technology - energy intensive fractional and extractive distillation
- Past patent literature shows the use of activated carbon/mole sieves technology* but does not have zeolite pore selectivity properties
- Other unmodified zeolite membranes rapidly deactivate from olefin & diolefin exposure

* US Patent Nos. 4,570,029 Kulprathipanja, S. , UOP Inc.; 3,596,436 Dassese, P., Solvay & Cie.

— Technical Section: Separations Methodology

Sandia IP for Modified Zeolite Technology, combined leads to *enhanced* HC selectivity:

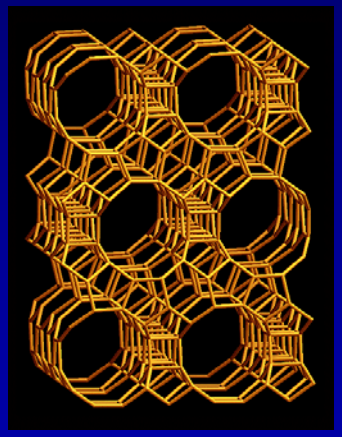
1) Molecular Sieving (pore size)

2) Adsorption Modification
(surface carbonization + acidity/reactivity)

3) Deactivation Stabilized
(high temp; multiple cycles)

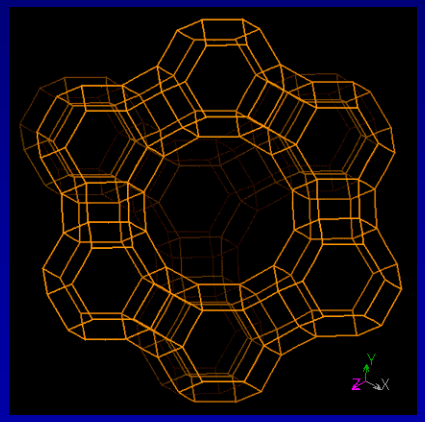
—Technical Section - Zeolites for Separations

	Relative acidity	Pore diameter (Å)
Zeolite β	high	6.6 x 7.7, 5.6
Zeolite-Y	medium-high	7.4
Zeolite-L	low	7.1
ZSM-5	high	5.1 x 5.5



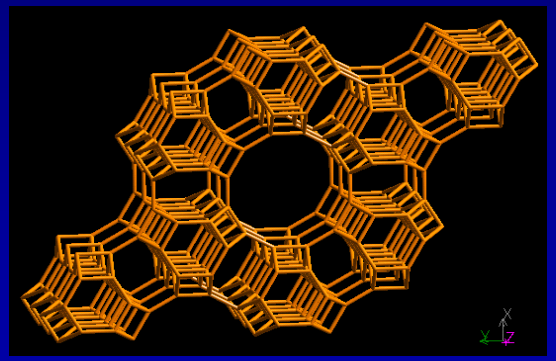
Zeolite-β

12 MR (3-D)
straight pores



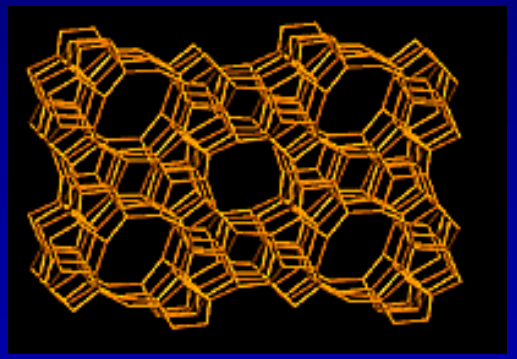
Zeolite-Y

12 MR (3-D, cages)
intersecting straight pores



Zeolite-L

12 MR (1-D)
straight pores



ZSM-5

10 MR (3-D)
Intersecting straight / sinusoidal pores

—Technical Section - Zeolite Modification (Acid site deactivated & pore size modified)

- ***Activating Zeolite:*** **The zeolites (crystalline molecular sieves) are regenerated at high temp to remove ancillary pore-blocking molecules.**

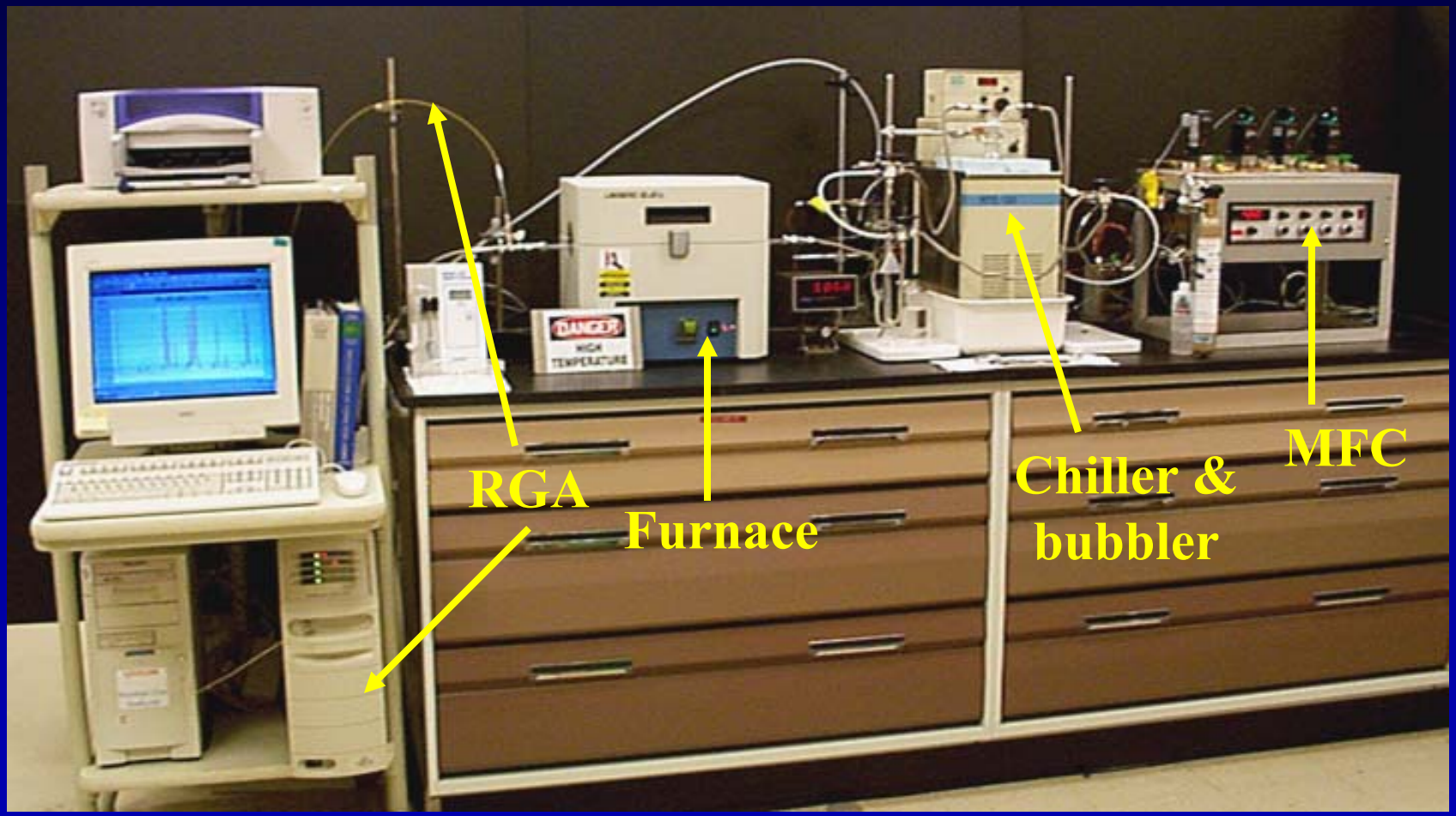
- ***Bulk Carbonization:*** **The regenerated zeolites are carbonized w/HC.**

hydrocarbon type/mixture, concentration, helium flow rate, exposure time, and temperature

- ***Temperature Programmed Desorption (TPD) Experiments:*** **The effect of bulk carbonization on the adsorptivity of the zeolites is assessed with temperature-programmed desorption experiment.**

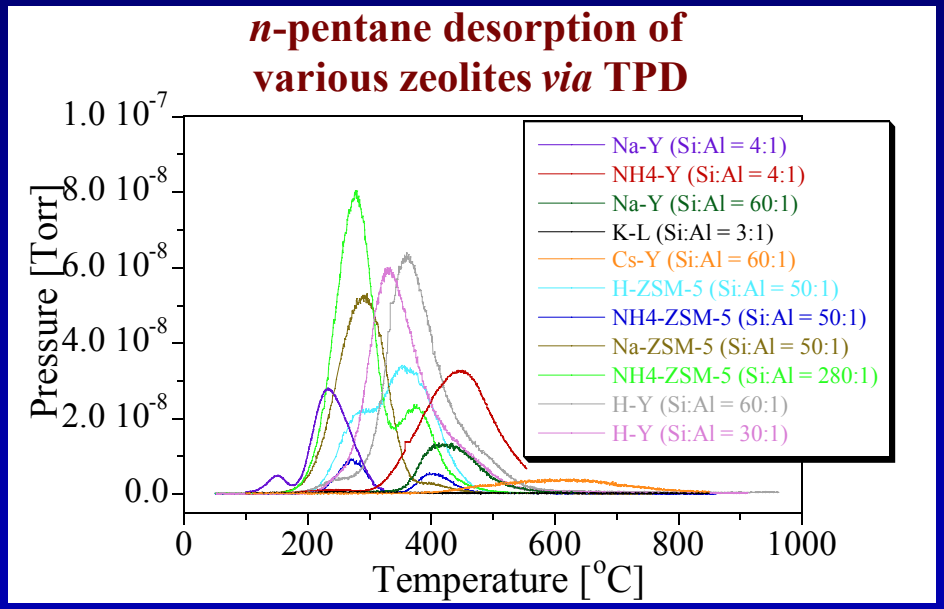
- ***Separation Experiments:*** **The carbonized zeolites are used for separation of a hydrocarbon from a hydrocarbon mixture.**

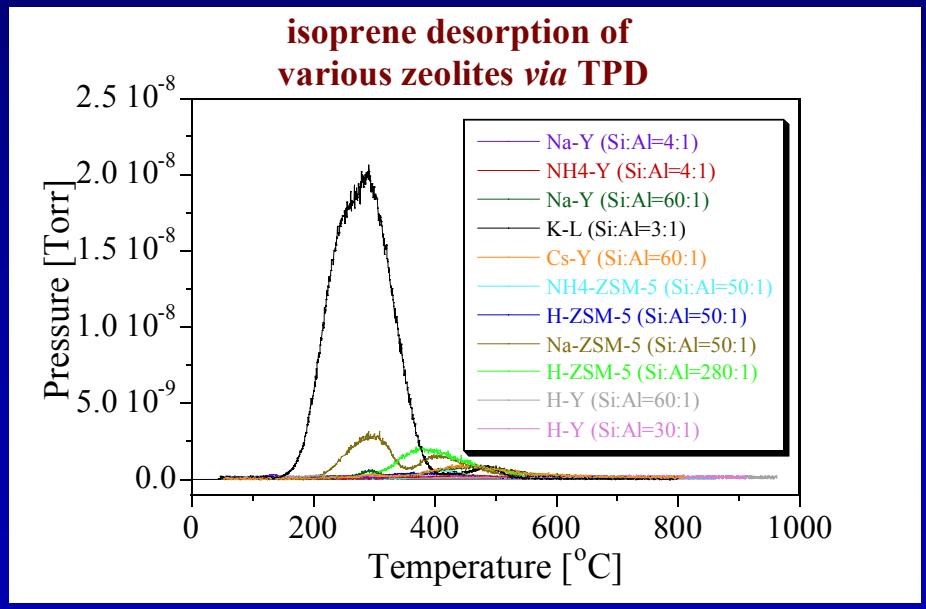
— Technical Section : In-house Sandia Reactor



— Technical Section : Surface Modification

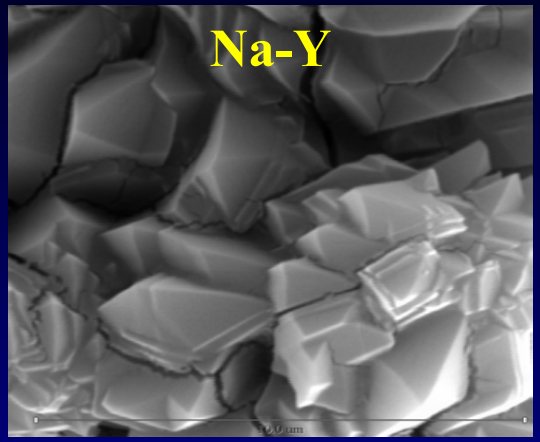
- *TPD experiments show that surface modification occurs at the active sites of the interior pores.*
- *Zeolite Y have selective adsorption for n-Pentane but no adsorption for Isoprene*

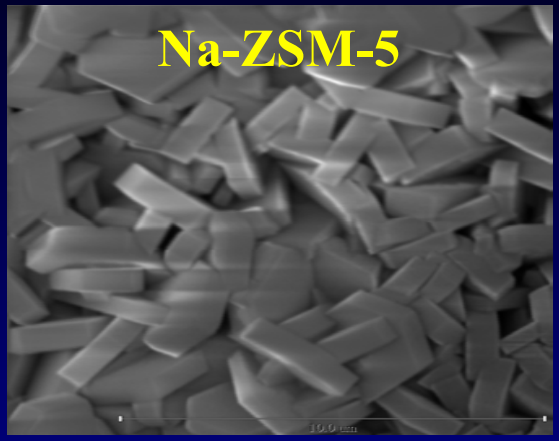


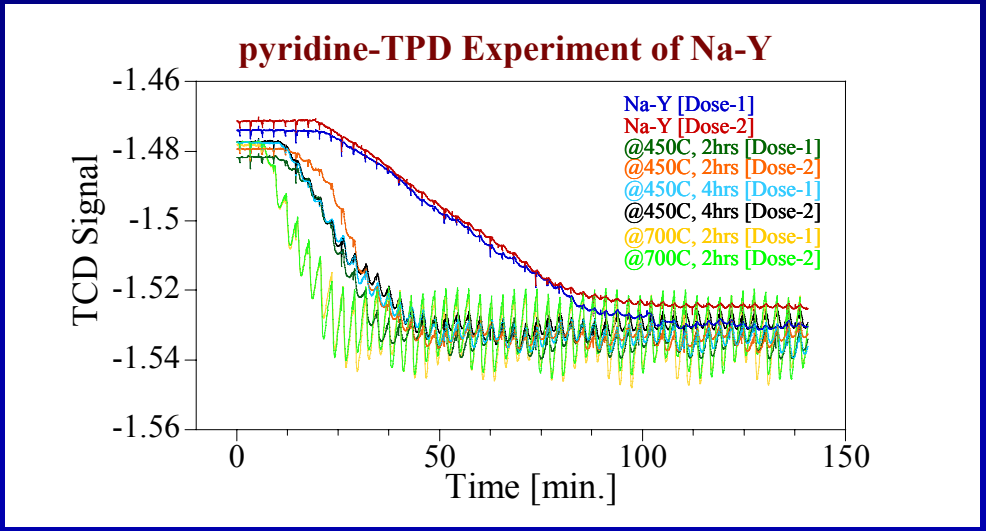


— Technical Section : Characterization Methods

- *PXRD*
- *SEM*
- *pyridine-TPD*
- *BET*







Goodyear Separation Unit

helium

MFC

Syringe
Pump

Zeolite
Membrane

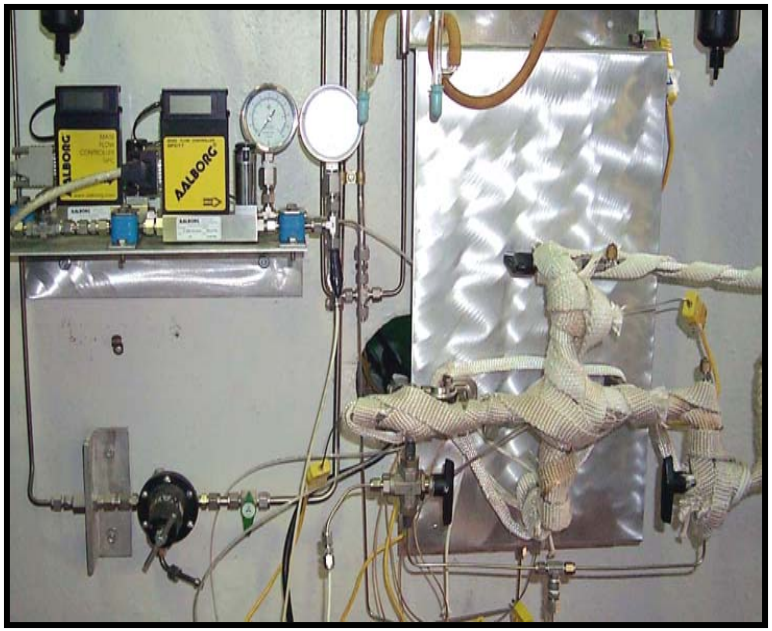
Permeate

Retentate

Helium sweep

MFC

On-line GC



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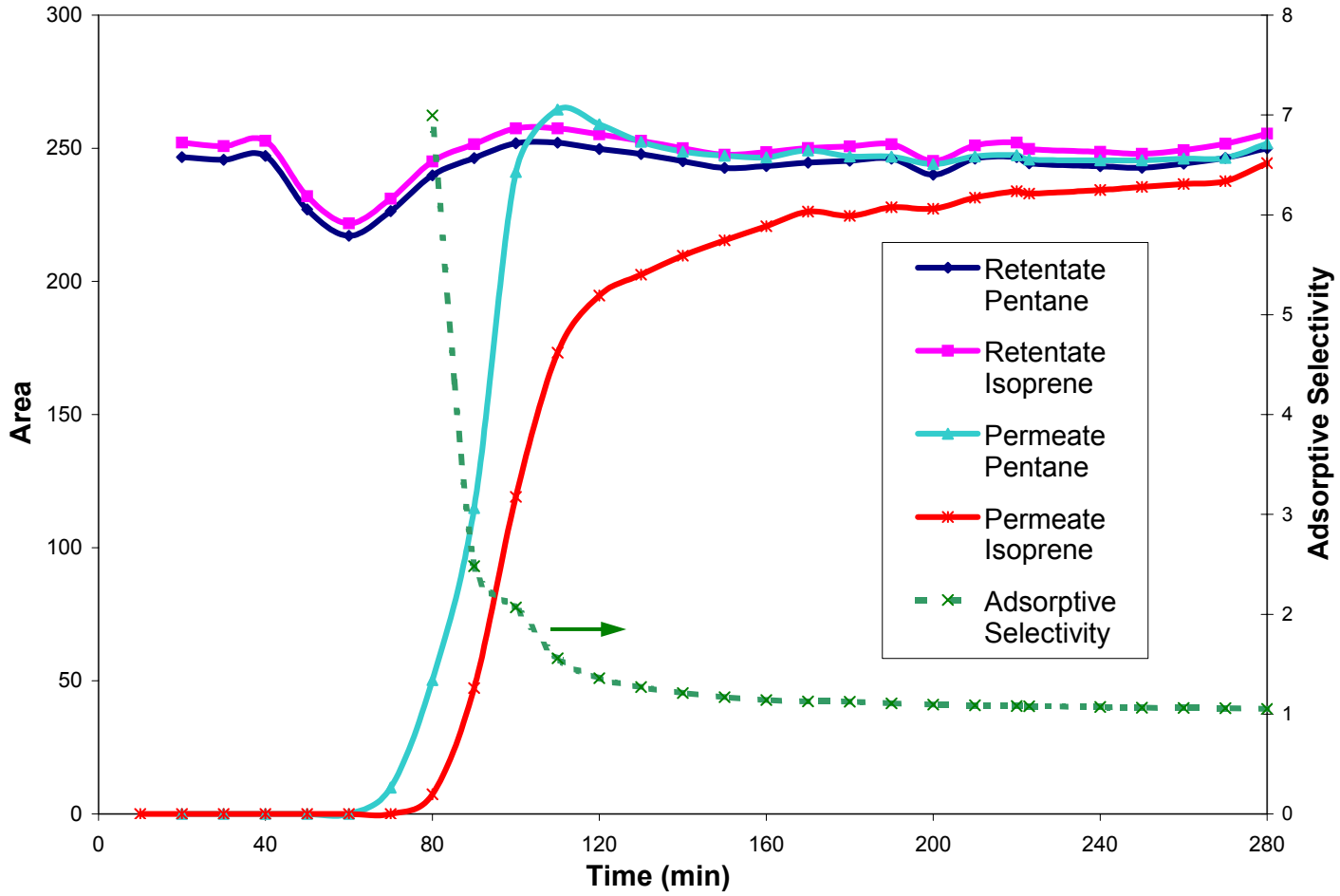
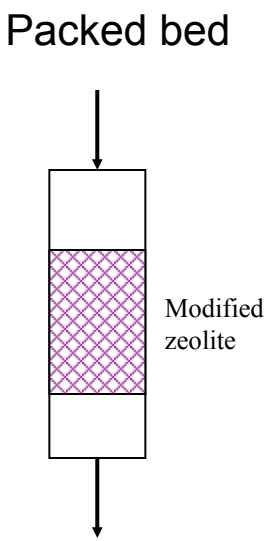
Experimental Results





Demonstrated isoprene/pentane separation using modified zeolite in dilute concentrations

Initial experiments show selectivity towards isoprene separation

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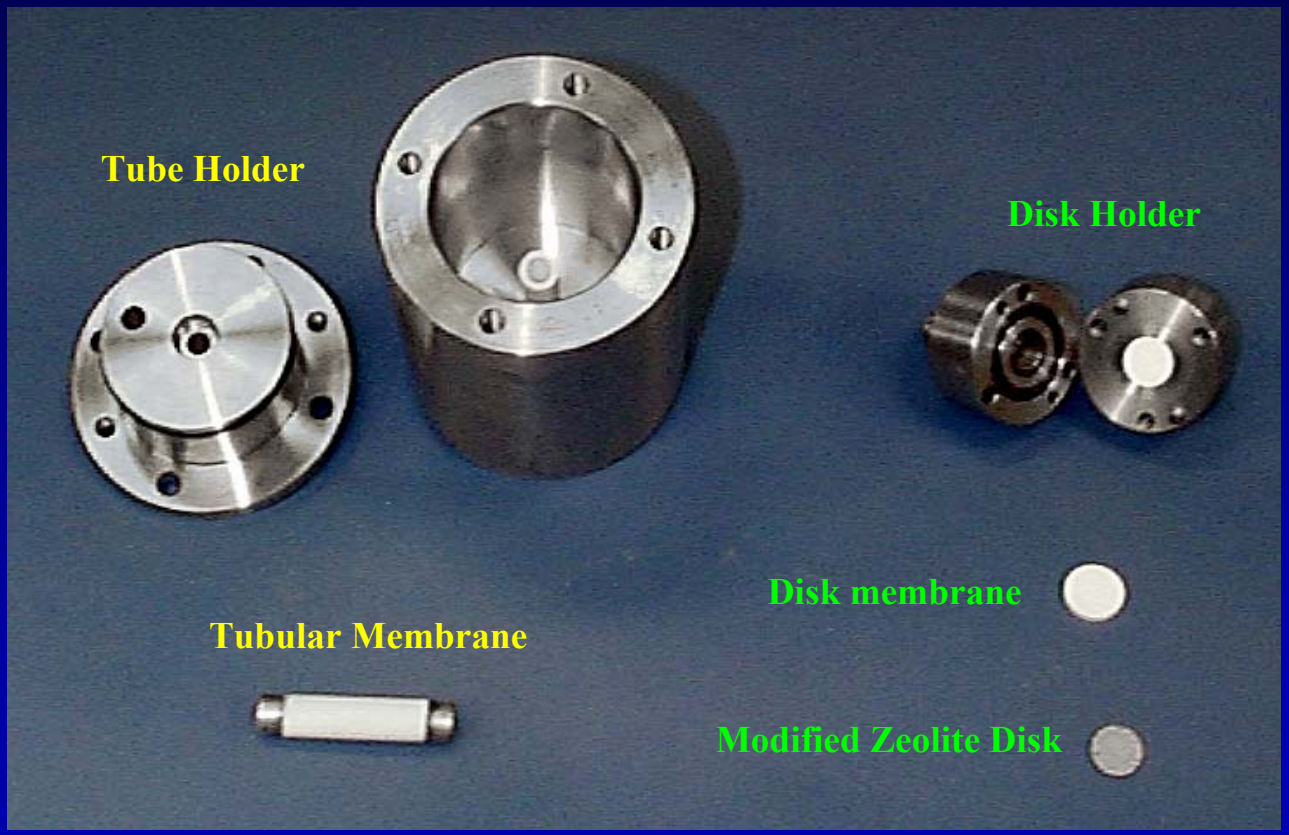
— Technical Section:
In-house Sandia Separation Unit

Test Unit

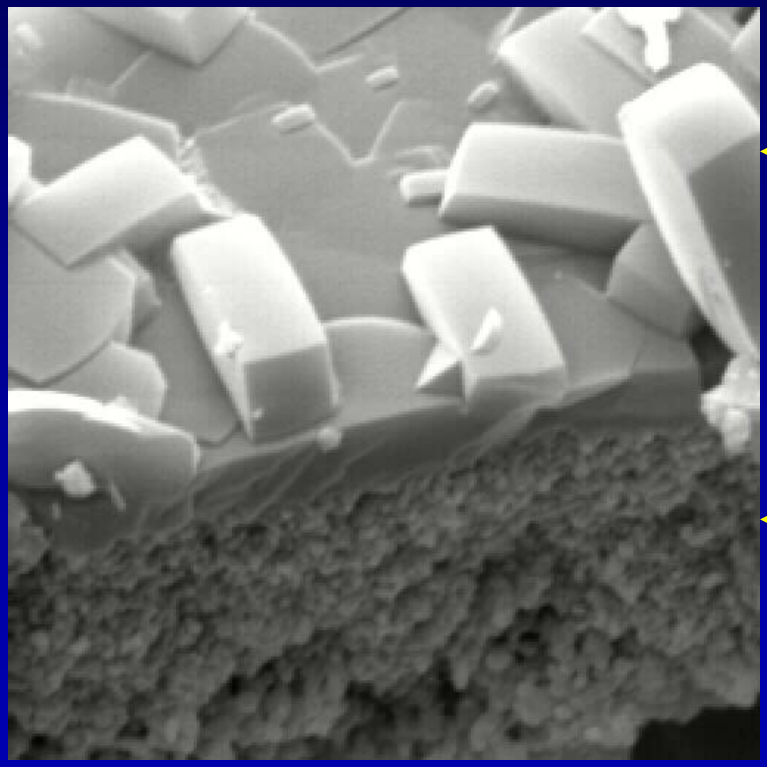
Test Cells

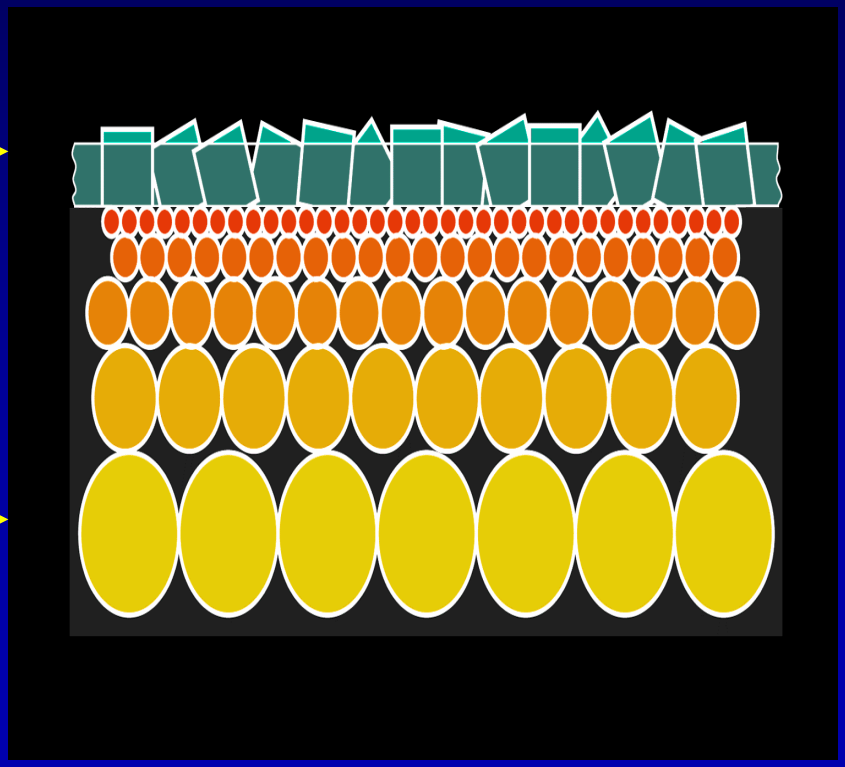


— Technical Section : Membrane Development

- *Na-Y and Na-ZSM-5 membranes have been produced*
- *Surface modification of the supported membranes are under way*

Crystalline Zeolite Membrane Layer (Selectively allows only specified Molecules to pass through)

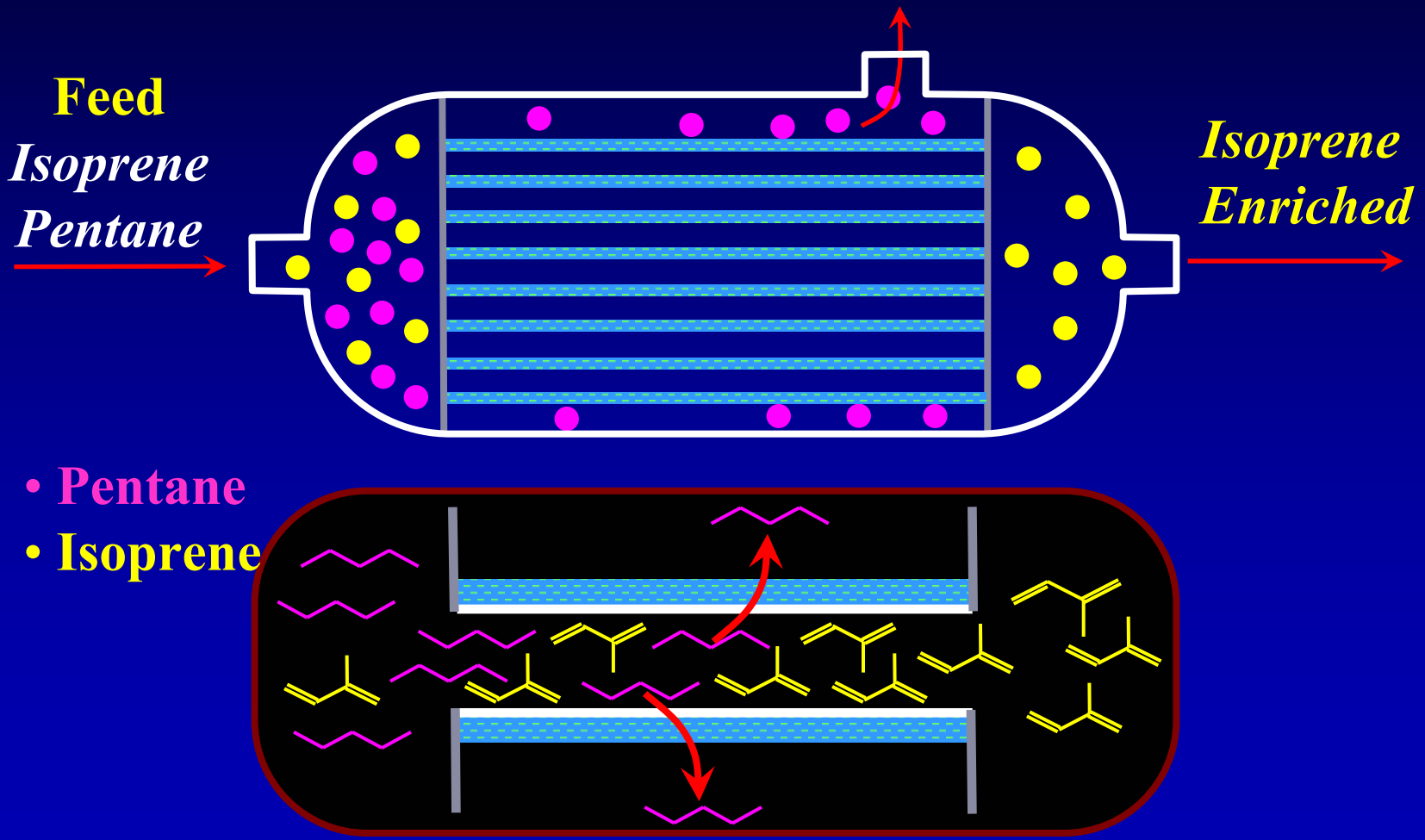




Support (allows all molecules to pass)

— Technical Section: Possible Module Design

Enhanced Selectivity: Molecular Sieving + Adsorption



— Summary : CRADA 1640.01 and IMF FY02

- Leveraged successful "Proof of Concept" FY01 in CRADA 1598 to a well funded winning DOE/OIT/IMF Proposal and New CRADA 1640.01
- DOE/OIT/IMF: Goodyear, Nofsinger, Sandia; $1.2M for 3 years; *50% industry in-kind contributions*
- Economic feasibility studies completed; point to successful implementation of modified zeolites for HC separations
- Bulk modification and adsorption studies show enhancement for isoprene versus n-pentane using modified zeolites (Y).
- New work to further enhance the fundamental knowledge and skills for isoprene purification for bulk and membranes.

— Acknowledgements

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the US DOE under Contract DE-AC04-94-AL85000.

Further Reading:

OFFICE OF INDUSTRIAL TECHNOLOGIES

http://www.oit.doe.gov/imf/factsheets/goodyr_zeolites.pdf

Supplemental Energy Benefits from IMF Project

Detailed Assumptions

- 22% Isoprene Energy Reduction
  - 1 % enrichment of isoprene which translates to 40,000,000 lbs. *LESS* raw materials processed to recover isoprene
- 64 Trillion Btu/yr Savings for C2-C5 Industry
  - Obtained 1997 production and energy consumption for C2-C5 industries from *DOE/OIT Energy & Environmental Profile of the U.S. Chemical Industry* - May 2000
  - Calculated Btu's/lb based on 1997 numbers
  - Multiplied Btu's/lb (1997) by 2002 estimated billion lbs/yr (CMAI) to get current C2-C4 energy consumption by process
  - Ignored energy consumption by downstream processes
    - ex. polyethylene, polypropylene, SBR, etc.